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(54) Dehydrogenation catalyst.

(57) Dehydrogenation catalyst comprising:
1 to 25% by weight of an alkali metal compound, calculated as stable alkali metal oxide,
0.5 to 20% by weight of a rare earth metal compound, calculated as the oxide,
0.1 to 10% by weight of a calcium compound, calculated as CaO,
0.5 to 10% by weight of a germanium-, tin- and/or lead compound, calculated as the dioxide, and
35 to 97.9% by weight of an iron compound, calculated as Fe_2O_3.

EP 0 297 657 A1

DEHYDROGENATION CATALYST

The invention relates to a dehydrogenation catalyst suitable for use in the dehydrogenation of hydrocarbons, especially in the dehydrogenation of ethylbenzene to styrene.

It is generally known that iron oxide containing catalysts are used in dehydrogenation reactions e.g. the conversion of ethylbenzene into styrene.

A number of catalysts have been described which are based on iron oxide, potassium oxide, together with other promoters such as cerium, chromium, molybdenum and calcium.

In French patent application 8519324 are disclosed a dehydrogenation catalyst mainly based on iron and an alkali metal, a rare earth metal and calcium as promoters, and a process for the dehydrogenation making use of the catalyst, e.g. a process for the preparation of styrene. Further prior art has also been discussed in the said French patent application.

It has now surprisingly been found that a dehydrogenation catalyst based on iron, alkali metal, rare earth metal and calcium can be further improved by containing an amount of germanium, tin or lead.

The invention accordingly relates to a dehydrogenation catalyst comprising:

1 to 25% by weight of an alkali metal compound, calculated as stable alkali metal oxide,

0.5 to 20% by weight of a rare earth metal compound, calculated as the oxide,

0.1 to 10% by weight of a calcium compound, calculated as CaO,

0.5 to 10% by weight of a germanium-, tin- and/or lead compound, calculated as the dioxide, and

35 to 97.9% by weight of an iron compound, calculated as Fe_2O_3.

More preferably the amount of calcium compound calculated as CaO is 0.5 to 10% by weight.

The invention is more so surprising since in a process described in French patent specification 7810760 a dehydrogenation catalyst based on iron was not improved by containing tin or lead. An improvement of the activity or selectivity of the catalyst could not be demonstrated.

The selectivity to a certain compound, expressed in a percentage, is defined herein as

$$\frac{a}{b} \times 100$$

wherein "a" is the amount of alkylbenzene that has been converted into that certain compound and "b" is the total amount of alkylbenzene that has been converted.

The alkali metal compounds which may be used in the process according to the present invention are those of lithium, sodium, potassium, rubidium and cesium. Very good results have been obtained with potassium compounds. The alkali metal compounds are present in the catalyst in an amount of from 1 to 25% by weight, preferably from 5 to 20% by weight, more preferably of from 6 to 15% by weight, calculated as alkali metal oxide. Suitable alkali metal compounds are the oxides, hydroxides and carbonates. Catalysts containing more than 25% by weight of an alkali metal compound have as a disadvantage that their bulk crushing strength is not very high.

The rare earth metals which may be used are lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium. Mixtures of rare earth metals may be used. Very good results have been obtained with cerium compounds.

The rare earth metal compounds are preferably present in the catalyst in an amount of 2 to 10% by weight, calculated as oxide in the highest valence state on the total catalyst.

It has been found that the presence of a calcium compound provides the extreme high stability of the catalyst being used in the dehydrogenation of hydrocarbons.

The calcium compound is present in an amount of 0.1 to 10% by weight, preferably 0.5 to 5% by weight, calculated as CaO.

The germanium-, tin- or lead compound is present in an amount of from 0.5 to 10% by weight, preferably in an amount of from 0.5 to 5% by weight, more preferably in an amount of from 0.8 to 4% by weight of the total catalyst and calculated on the dioxide.

Of said three beforementioned compounds tin dioxide is the most preferred.

According to a preferred embodiment of the catalyst of the present invention the weight ratio of SnO_2 and CeO_2 $\leq$1:2 is applied Specific embodiments of the catalyst compositions of the present invention show total pore volumes varying in the range of from 0.34 to 0.27 cm^3/g and median pore diameters in the range of from 400 to 575 nanometer, although these parameters have not been found to be critical.

An attractive feature is that the present catalyst does preferably not need to contain molybdenum, tungsten or vanadium in order to reach the same level of selectivity.

The dehydrogenation process is suitably carried out using a molar ratio steam to alkylbenzene in the range of from 2 to 20 and preferably of from 5 to 13. Another attractive feature is that relatively low molar

ratios steam to alkylbenzene can be used.

The dehydrogenation processes are suitably carried out at a temperature in the range of from 500 °C to 700 °C. An attractive feature of the process is that relatively low temperatures can be used, particularly in the range of from 550 °C to 625 °C.

The dehydrogenation processes may be carried out at atmospheric or super- or subatmospheric pressure. Atmospheric pressure and pressures between 1 bar and 0.5 bar absolute are usually very suitable.

The dehydrogenation processes are suitably carried out using a liquid hourly space velocity in the range of from 0.1 to 5.0 litre of alkylbenzene per litre of catalyst per h, using, for example, a tubular or radial flow reactor.

An alkylbenzene may be used as a starting compound in the dehydrogenation process and has suitably 2 or 3 carbon atoms in the alkyl group. Very good results have been obtained with ethylbenzene. Isopropylbenzene is another example of a starting compound. If desired, the aromatic nucleus in the alkylbenzene may carry a second substituent, for example a methyl group.

The catalyst may be used in the form of, for example, pellets, tablets, spheres, pills, saddles, trilobes or tetralobes.

The iron oxide to be used for the preparation of the novel catalysts may be, for example, hydrated or not-hydrated Fe_2O_3. The iron oxide may be a synthetically produced, powdered red, red-brown, yellow or black pigment. The red or red-brown pigments are highly pure ferric oxide, while the black pigment is the magnetic form, ferrosoferric oxide (Fe_3O_4), which is usually found in the catalyst under various reaction conditions. The yellow iron oxides consist of the monohydrated form of ferric oxide. These oxides are prepared by various methods, for example oxidation of iron compounds, roasting, precipitation, calcination, and the like. A suitable form of iron compound is the mono-hydrated yellow iron oxide used in the preparation of catalysts according to US patent specifications 3,360,597 and 3,364,277. Particularly suitable are pigment grade red iron oxides of purities exceeding 98% by weight. These red oxides have surface areas ranging from 2 to 50 m^2/g. The alkali metal compound, the rare earth metal compound, e.g. cerium compound, calcium compound and tin compound may be brought onto the iron oxide in any suitable manner, for example by intimate mixing iron oxide with a suitable alkali metal compound, a suitable cerium compound, a suitable calcium compound and a suitable tin compound in the presence of water. The mixture obtained may be dried and then calcined at a temperature in the range of from, for example, 500 °C to 1200 °C.

Suitable alkali metal compounds are, for example, carbonates, hydrogen carbonates, nitrates and acetates; suitable cerium compounds are, for example, cerium nitrate, cerium carbonate and cerium acetate; suitable calcium compounds are calcium nitrate, calcium carbonate, calcium acetate and calcium isobutyrate.

Suitable germanium-, tin- or lead compounds are, for example, sulphates, nitrates, carbonates, acetates and oxides of these metals. Also stannates, germanates and plumbates are suitable.

Catalysts having a highly porous structure and a low surface area are highly active in catalytic dehydrogenation. Various methods may be employed to form highly porous catalysts. For example, combustible materials, such as sawdust, carbon, wood flour, etc., may be added during catalyst formation, and then burned out after the pellet has been formed. Many of these porosity-promoting aids also assist in facilitating extrusion of pellets, for example, the use of graphite, potassium alginate and aqueous solutions of methyl cellulose.

If desired, the catalyst may be used supported on a carrier, for example zinc aluminate.

The following examples further illustrate the invention.

EXAMPLE 1 Non contiene ossido di molibdeno

A dehydrogenation catalyst (catalyst 1) containing 79.6 %wt Fe_2O_3, 11 %wt K_2O, 6.8 %wt CeO_2, 1.2 %wt SnO_2 and 1.4 %wt CaO, was prepared as follows. An intimate mixture was prepared starting from red iron oxide (unhydrated), potassium carbonate, cerium carbonate, tin dioxide, calcium carbonate and potassium alginate with gradual addition of water during mixing. The paste obtained was extruded and pelletized to cylindrical particles having a diameter of 3 mm and a length of 5 mm. The cylinders were dried for 2 h at 75 °C and 3 h at 110 °C and then calcined for 2 h at 800 °C and then allowed to adopt ambient temperature.

A mixture of ethylbenzene and steam heated to a certain temperature, was introduced into a reactor and lead over 100 ml of catalyst, prepared as described above.

The mixture was conducted at a certain pressure and a certain liquid hourly space velocity through the catalyst bed.

The temperature was adjusted so that the conversion of ethylbenzene was 70%. The reaction product leaving the reactor was analyzed by means of gas-liquid chromatography. From the data obtained the temperature at 70% ethylbenzene conversion and the selectivity to styrene was calculated.

The steam to ethylbenzene molar ratios were different in the experiments, viz. 12, 8 and 6.5. The temperature (T_{70}) of the catalyst was adjusted until the conversion of ethylbenzene was 70%. The selectivity to styrene at 70% conversion is indicated as S_{70}.

The stability of the catalysts was determined at a molar ratio steam to ethylbenzene of 6.5 by determining the average increase of the temperature which was necessary to keep the conversion of ethylbenzene at the constant value in each experiment. This average increase of temperature is indicated as "°C/day".

The respective T_{70}- and S_{70}-values are given in Tables III-VI.

EXAMPLE 2

In about the same way as described in Example 1, dehydrogenation catalysts were prepared the compositions of which are mentioned in the subsequent Table I.

TABLE I

Catalyst	K_2O %wt	CeO_2 %wt	CaO %wt	SnO_2 %wt	XOy %wt	FeO_3 %wt
2	11	6.8	1.4	0.6	-	80.2
3	11	6.8	0.2	1.2	-	80.8
4	11	6.8	0.6	0.5	-	81.1
5	11	6.8	1.0	0.9	-	80.3
6	11	6.8	1.4	5.0	-	75.8
7	11	6.8	1.4	-	0.8 GeO_2	80.0
8	11	6.8	1.4	-	1.8 PbO	79.0
9	10.25	6.8	1.4	1.95 K_2SnO_3	-	79.6

These catalyst compositions were tested with reference to the conversion of ethylbenzene and steam, as described in Example 1.

The specific conditions and test results have been summarized in Tables III-VI.

COMPARATIVE EXAMPLE

In about the same way as described in Example 1 comparative dehydrogenation catalysts were prepared, the compositions of which are mentioned in the subsequent Table II:

TABLE II

Catalyst	K_2O %wt	CeO_2 %wt	CaO %wt	SnO_2 %wt	XOy %wt	FeO_3 %wt
A	11	6.8	-	1,2	-	81.0
B	11	-	1.4	1.2	-	86.4
C	11	6.8	1.4	-	1.2 Sb_2O_4	79.6
D	11	6.8	1.4	-	1.9 Bi_2O_3	78.9
E	11	6.8	1.4	-	-	80.8

These catalyst compositions were tested with reference to the conversion of ethylbenzene and steam,

as described in Example 1. The specific conditions and test results have been summarized in Tables III-VI.

TABLE III

Experiments using 100 cm³ extrudates 5 mm x ϕ 3 mm LHSV = 0.65 h^{-1}

Catalyst	1 atm steam/ethylbenzene ratio = 12		0.75 atm steam/ethylbenzene ratio = 8		575 °C steam/ethylbenzene ratio = 6.5
	T_{70}	S_{70}	T_{70}	S_{70}	°C/day
1	611	94.1	610.5	95.5	2.3
2	-	-	608.5	94.8	2.0
9	614	93.5	619	95.0	-
E	608	92.3	605	93.6	3.0

TABLE IV

Experiments using 100 cm³ extrudates 5 mm x ϕ 3 mm LHSV = 0.65 h^{-1}

Catalyst	1 atm pressure	steam/ethylbenzene ratio = 12		0.75 atm	steam/ethylbenzene ratio = 8
	T_{70}	S_{70}	compared selectivity (*) %	T_{70}	S_{70}
1	611	94.1	95.1	610.5	95.5
4	602	93.1	94.6		
5	610	93.2	94.5	605	95.1

It will be appreciated that test results of catalysts are summarized having constant K_2O and CeO_2 contents and varying contents of SnO_2 and CaO.

(*) Selectivities are compared at a given conversion, 16.5 points lower than the max. conversion at thermodynamic equilibrium.

TABLE V

Test results with microflow unit: 10 cm^3 of crushed catalyst: LHSV = 1 h^{-1}			
Catalyst	1 atm	steam/ethyl-benzene ratio =	Compared Selectivity (*) %
	T_{70}	S_{70}	
1	611.5	95.05	95.7
7	607	94.4	95.4
8	608.5	94.8	95.1
C	> 640	-	-
D	608	93.85	94.9
It will be appreciated that in this table the test results are combined of catalysts containing as promoters: 11% K_2O, 6.8% CeO_2, 1.4% CaO and XO_y.			

(*) Selectivities are compared at a given conversion, 16.5 points lower than the max. conversion at thermodynamic equilibrium.

TABLE VI

Experiments using 100 cm^3 extrudates 5 mm x Ø 3 mm LHSV = 0.65 h^{-1}				
Catalyst	1 atm	steam/ethyl-benzene ratio = 12	Compared Selectivity (*) %	Stability at steam/ethyl-benzene ratio = 12
	T_{70}	S_{70}		
1	611	94.1	95.1	stable
3	610	92.2	93.6	stable
A	610	91.3	92.7	less stable
B	-	-	92.0	unstable

(*) Selectivities are compared at a given conversion, 16.5 points lower than the max. conversion at thermodynamic equilibrium.

Claims

1. Dehydrogenation catalyst comprising:
1 to 25% by weight of an alkali metal compound, calculated as stable alkali metal oxide,
0.5 to 20% by weight of a rare earth metal compound, calculated as the oxide,
0.1 to 10% by weight of a calcium compound, calculated as CaO,
0.5 to 10% by weight of a germanium-, tin- and/or lead compound, calculated as the dioxide, and
35 to 97.9% by weight of an iron compound, calculated as Fe_2O_3.
2. Dehydrogenation catalyst according to claim 1, comprising:
1 to 25% by weight of an alkali metal compound, calculated as stable alkali metal oxide,
0.5 to 20% by weight of a rare earth metal compound, calculated as the oxide,

0.5 to 10% by weight of a calcium compound, calculated as CaO,

0.5 to 1.0% by weight of a germanium-, tin- and/or lead compound, calculated as the dioxide, and

35 to 97.9% by weight of an iron compound, calculated as Fe_2O_3.

3. Dehydrogenation catalyst according to claims 1 and 2 characterized in that it comprises tin dioxide.

4. Dehydrogenation catalyst according to any one of the claims 1-3 characterized in that the weight ratio of SnO_2 and CeO_2 $\leqq 1:2$.

5. Dehydrogenation catalyst as claimed in any one of the claims 1-4, wherein the alkali metal compound is a potassium compound.

6. Dehydrogenation catalyst as claimed in any one of the claims 1-5, wherein the rare earth metal is cerium.

7. Dehydrogenation catalyst as claimed in any one of the claims 1-6, wherein the amount of rare earth metal compound lies in the range of from 1 to 10% by weight.

8. Dehydrogenation catalyst as claimed in any one of the claims 1-7, wherein the amount of alkali metal compound lies in the range of from 6 to 15% by weight.

9. Dehydrogenation catalyst as claimed in any one of the claims 1-8, wherein the amount of calcium compound lies in the range of from 0.5 to 5% by weight.

10. Dehydrogenation catalyst as claimed in any one of the claims 1-9, wherein the amount of tin compound lies in the range of from 0.5 to 5% by weight.

11. Dehydrogenation catalyst as claimed in claim 10, wherein the amount of tin compound lies in the range of from 0.8 to 4% by weight.

12. Dehydrogenation catalyst as claimed in claim 1, as hereinbefore described with special reference to examples 1 and 2.

13. A process for the preparation of styrene wherein a mixture of ethylbenzene and steam is contacted at a temperature between 500° C and 700° C with a dehydrogenation catalyst as claimed in any one of the claims 1-11.

14. Styrene whenever prepared by means of a process as claimed in claim 13.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 88 20 1284

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	EP-A-0 181 999 (SÜD CHEMIE AG) ---		B 01 J 23/82 C 07 C 5/333 C 07 C 15/46
A	FR-A-2 266 738 (COMPAGNIE FRANCAISE DE RAFFINAGE) ---		
A	US-A-4 460 706 (IMANARI et al.) ---		
D,A	US-A-3 364 277 (SIEM) ---		
D,P A	FR-A-2 592 375 (SHELL) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			B 01 J C 07 C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14-09-1988	LO CONTE C.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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